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The Magnetic Properties of the Copper(II) Alkanoate Adducts with Benzimidazole and Related Nitrogen Donors

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Synopsis. Various copper(II) alkanoate adducts with benzimidazole, *N*-acetylbenzimidazole, and benzoxazole have been prepared. The influence of the hydrogen bonded structure in the benzimidazole adducts on their magnetic properties are discussed.

A number of magnetic studies concerning dinuclear copper(II) carboxylates have revealed that the magnitude of the spin-exchange coupling between copper(II) ions is affected by the donor characteristics of both the bridging carboxylato and axial donor ligands.[1-3] For example, the room-temperature magnetic moments of the copper(II) alkanoate adducts with cyclic tertiary amines and cyclic ethers can be expressed according to

$$\mu_{\text{eff}} = -0.052(\text{p}K_\text{a} - 0.068\text{p}K_\text{a}' - 4.56) + \Delta\mu_\alpha + 1.38_5, \qquad (1)$$

where pK_a and pK_a' are the acidities of the conjugate acids of alkanoate and axial ligands, respectively. $\Delta\mu_\alpha$ is the correction term for the substitution in the methyl group of acetic acid (-0.05_8 and -0.07_0 BM for the series of mono- and disubstituted acetates, respectively),[4] including the corrections for steric strain, field effect, and hyperconjugation.[4] Also, for the hydrates[1,5,6] and the ammonium chloride adducts,[7-9] a similar relationship can be demonstrated by plots of their corrected magnetic moments, $\mu_{\text{eff}}-\Delta\mu_\alpha$, against p$K_\text{a}$$-$0.068p$K_\text{a}'$, when -7.0 and -1.74 are used for the pK_a' values of chloride ion[10] and water molecule, respectively. However, the intercept obtained in this way (1.39_9 BM at pK_a=4.56 and pK_a'=0) is slightly larger than that in Eq. 1. This difference seems to be caused by the following two structural backgrounds: (1) the hydrogen bonding between the carboxylato oxygen atom and the neighboring proton donor, such as ammonium ion or water molecule,[11,12] decreases the electron density on the oxygen atom, and (2) the steric repulsion resulting from the bulky nature of the axial ligand, such as tertiary amines,[13] weakens its coordination bond. In order to clarify which factor plays a more important role in the above difference, we carried out preparations and magnetic susceptibility measurements of the copper(II) alkanoate adducts with benzimidazole, *N*-acetylbenzimidazole, and benzoxazole. These compounds are appropriate for studying the effect of hydrogen bonding on their magnetic properties, since all of these ligands have a similar bulkiness around their coordination sites, while only the benzimidazole adducts have hydrogen-bonded structures.[14,15]

Benzimidazole and benzoxazole are commercially available and were used without further purification.

Table 1. Analytical Data and Effective Magnetic Moments at 20 °C

Compound	Found(Calcd)/%				μ_{eff}/BM
	Cu	C	H	N	
$Cu(C_2H_5COO)_2\cdot C_7H_6N_2$	19.63 (19.38)	47.02 (47.63)	4.93 (4.92)	8.05 (8.55)	1.33
$Cu(C_3H_7COO)_2\cdot C_7H_6N_2$	18.08 (17.86)	50.35 (50.63)	5.64 (5.66)	7.74 (7.87)	1.34
$Cu(ClCH_2CH_2COO)_2\cdot C_7H_6N_2$	15.79 (16.02)	39.13 (39.36)	3.63 (3.56)	6.81 (7.06)	1.37
$Cu(C_2H_5COO)_2\cdot C_7H_5NO$	19.41 (19.33)	47.14 (47.49)	4.63 (4.60)	4.08 (4.26)	1.31
$Cu(C_3H_7COO)_2\cdot C_7H_5NO$	17.69 (17.81)	50.37 (50.49)	5.35 (5.37)	3.87 (3.92)	1.30
$Cu(ClCH_2CH_2COO)_2\cdot C_7H_5NO$	15.95 (15.98)	39.14 (39.26)	3.27 (3.29)	3.51 (3.52)	1.35
$Cu(ClCH_2COO)_2\cdot C_7H_5NO$	17.23 (17.19)	35.16 (35.74)	2.48 (2.45)	3.68 (3.79)	1.42
$Cu(CH_3CHClCOO)_2\cdot C_7H_5NO$	16.23 (15.98)	39.07 (39.26)	3.18 (3.29)	3.47 (3.52)	1.41
$Cu(C_2H_5COO)_2\cdot C_9H_8N_2O$	17.12 (17.18)	48.42 (48.71)	4.90 (4.91)	7.62 (7.57)	1.31
$Cu(C_3H_7COO)_2\cdot C_9H_8N_2O$	15.98 (15.97)	51.28 (51.31)	5.55 (5.57)	7.05 (7.04)	1.30
$Cu(ClCH_2CH_2COO)_2\cdot C_9H_8N_2O$	14.43 (14.48)	40.99 (41.06)	3.71 (3.68)	6.36 (6.38)	1.34
$Cu[(CH_3)_2CHCOO]_2\cdot C_9H_8N_2O$	16.06 (15.97)	51.27 (51.31)	5.53 (5.57)	6.93 (7.04)	1.31
$Cu(CH_3CHClCOO)_2\cdot C_9H_8N_2O$	14.53 (14.48)	41.09 (41.06)	3.69 (3.68)	6.44 (6.38)	1.41

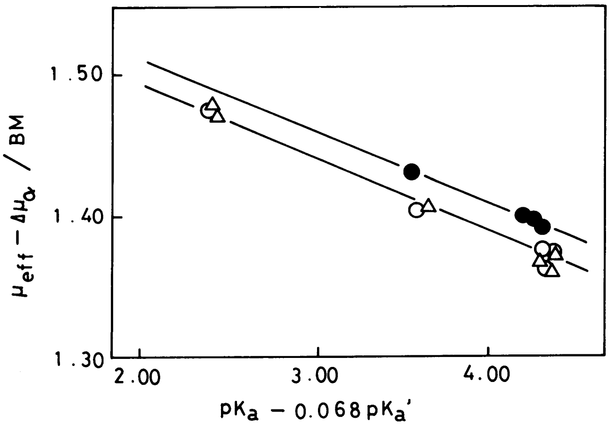

Fig. 1. The corrected magnetic moments at 20 °C plotted against the acidities of the ligands for the copper(II) alkanoate adducts with benzimidazole (●), *N*-acetylbenzimidazole (○), and benzoxazole (△).

N-Acetylbenzimidazole was prepared by the procedure of Reddy et al., mp 113 °C (lit, mp 113 °C).[17] Various copper(II) alkanoate adducts were obtained by a general procedure for synthesizing adducts with heterocyclic amines.[16,18]

The effective magnetic moments of these compounds (Table 1) were evaluated from the room-temperature magnetic susceptibilities, which were corrected for the diamagnetism of the ligands using Pascal constants,[19] and for $N\alpha$ using 60×10^{-6} emu mol^{-1} (1 emu=$4\pi\times10^{-6}$ m^3). The IR spectra of these compounds show characteristic bands in the ranges 1675—1615 and 1435—1405 cm^{-1} associated with unsymmetric and symmetric COO stretching vibrations of the carboxyl groups.[21] In the crystal of the copper(II) acetate adduct with benzimidazole, its dinuclear structure and the interdinuclear hydrogen-bond contact between the carboxylato oxygen atom and the benzimidazole ligand have been established by an X-ray analysis.[14] The magnetic and IR spectral data indicate that the present compounds also have bridged dinuclear structures similar to that of copper(II) acetate monohydrate.[11,12] In addition, the broad NH stretching bands[22] at about 3250—3200 cm^{-1} indicate that hydrogen bonding is involved in the benzimidazole adducts.

In order to confirm the linear correlation, the corrected magnetic moments, $\mu_{eff}-\Delta\mu_{\alpha}$, of the present compounds together with those of the corresponding acetates,[15,18] are plotted against $pK_a-0.068pK_a'$ in Fig. 1, using the pK_a' value of 5.46, 4.74, and 3.96, (the last two values are estimated by the Branch-Calvin equation[23]) for benzimidazole, *N*-acetylbenzimidazole, and benzoxazole, respectively. The error in the estimation of pK_a' values is practically permissible, since the coefficient of pK_a' in Eq. 1 is very small. As can be seen from Fig. 1, the points for the benzimidazole adducts and the rest are on different lines from each other, which have the same slope of −0.052 BM and intercepts of 1.37$_9$ and 1.36$_3$ BM, respectively. The intercepts obtained here are somewhat smaller than that of Eq. 1, and may be explained in terms of a steric hindrance for axial ligation. However, the present ligands have a similar bulkiness around the donor atoms. Thus, the difference in the intercepts apparently indicates the effect of hydrogen bonding in the benzimidazole adducts. The reported singlet–triplet separation values for the benzimidazole and benzoxazole adducts of copper(II) acetate (324 and 344 cm^{-1} respectively)[15,18] indicate that the hydrogen bonding weakens the intradinuclear antiferromagnetic interaction. The magnitude of the difference (ca. 0.01$_5$ BM) is comparable to that of the difference between the tertiary amine adducts and the ammonium chloride adducts of copper(II) alkanoate. Although both the strength and number of hydrogen bonds have been disregarded, this coincidence indicates that the difference between those of the tertiary amine and the ammonium chloride adducts is mainly attributable to hydrogen bonding and that the steric hindrance to an axial coordination of the tertiary amines is negligible, probably due to considerably long sp^3 hybridized orbitals at their coordination sites.

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